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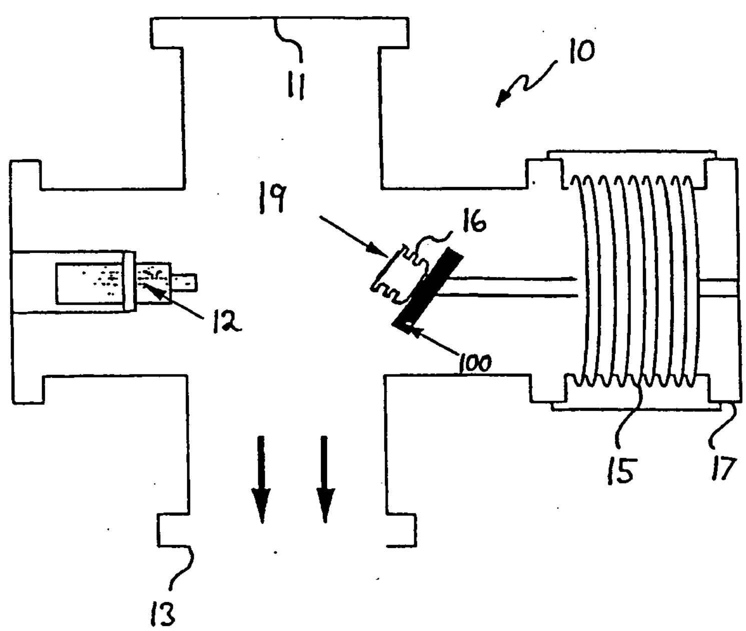
(54) Title: EPITAXIAL FILMS



(57) Abstract: Growth of epitaxial zinc sulphide semiconductor film using zinc diethyldithiocarbamate precursor as single source.

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EPITAXIAL FILMS

Field of the Invention

The present invention relates broadly to the growth of epitaxial II-VI semiconductor films. The invention will be described herein with reference to the growth of epitaxial zinc sulfide (ZnS) on silicon (Si) (111) substrates, but it will be appreciated that the invention does have broader applications relating to growth of epitaxial II-VI semiconductor films of different materials and/or on different substrates.

Background of the Invention

Films that grow with singular crystallographic orientation in all directions are referred to as epitaxial films. This has to be contrasted with poly-crystalline thin films, which include a large number of crystallites but with variable orientations with respect to each other.

Epitaxial thin films have been produced using a variety of different techniques, including molecular beam epitaxy (MBE), vapour phase epitaxy (VPE) and atomic layer epitaxy (ALE). However, a common characteristic of those techniques is that the epitaxial film growth requires multiple sources for the film elements, for example separate sources for zinc (Zn) and sulphur (S) are required for the epitaxial growth of ZnS films. Therefore, such techniques can have the disadvantage of being rather complex processes, during which a large number of variables must be controlled. This often results in high costs associated with the operation of machines for epitaxial film growth.

Epitaxial thin films are desirable for a large number of applications including light emitting layers for diodes, as active layers in optical/electro-optical thin film devices and as coatings. In this application, the single-crystal like characteristics of epitaxial films are utilised, which are typically superior to the characteristics of polycrystalline films.

Summary of the Invention

In accordance with a first aspect of the present invention there is provided an epitaxial II-VI semiconductor film grown using single source chemical vapour deposition.

In one embodiment, the epitaxial film comprises ZnS.

Preferably, the ZnS is grown using zinc diethyldithiocarbamate as precursor for the single source chemical vapour deposition.

In another preferred embodiment, the ZnS is grown using $Zn(S_2CNR_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

The number of carbon atoms in the alkyl group is preferably in the range from 1 to 6.

In accordance with a second aspect of the present invention there is provided a process comprising the steps of utilising single source chemical vapour deposition for growing an epitaxial II-VI semiconductor film on a substrate.

In one embodiment, the epitaxial film comprises ZnS.

In one preferred embodiment the process comprises the use of zinc diethyldithiocarbamate as a precursor for the single source chemical vapour deposition.

In another preferred embodiment, the ZnS is grown using $Nz(S_2CNR_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

The number of carbon atoms in the alkyl group is preferably in the range from 1 to 6.

Preferably, the substrate comprises a silicon (111) substrate.

In accordance with a third aspect of the present invention, there is provided a substrate coated with a coating comprising an epitaxial II-VI semiconductor film grown using single source chemical vapour deposition.

Preferably, the substrate comprises silicon (111).

In one embodiment, the epitaxial film comprises ZnS.

In accordance with a fourth aspect of the present invention, there is provided a process for growing an epitaxial II-VI semiconductor film, the process comprising the steps of cleaning a substrate, heating the substrate to a deposition temperature, the sublimation of a single source chemical vapour deposition precursor;

the pyrolysis of the precursor molecules on the heated substrate; and

the formation of the epitaxial film on the heated substrate.

Preferably, the substrate comprises silicon (111).

In one embodiment, the epitaxial film comprises ZnS.

Preferred forms of the invention will now be described, by way of example only, with reference to the accompanying drawings.

Brief Description of the Drawings

Figure 1 is a schematic drawing of a deposition chamber embodying the present invention.

Figure 2 shows angle dependent X-ray photoelectron defraction measurements of epitaxial films embodying the present invention.

Figure 3 is schematic drawing illustrating a side view of a ZnS crystalline structure.

Figure 4 shows an X-ray photoelectron spectroscopy wide scan of a ZnS film embodying the present invention.

Figure 5 shows an angle dependent X-ray photoelectron defraction measurements of a ZnS film after sputtering.

Figure 6 shows energy dependent X-ray photoelectron defraction measurements of an epitaxial film embodying the present invention.

Figure 7 is schematic drawing illustrating a side view of a ZnS crystalline structure.

Figure 8 is a schematic drawing illustrating the formation of an epitaxial film embodying the present invention.

Figure 9 is a block diagram illustrating the growth of epitaxial films embodying the present invention.

Figure 10 is a schematic diagram illustrating a device application embodying the present invention.

Detailed Description of the Preferred Embodiments

In Figure 1, a high vacuum deposition chamber 10 (base pressure 10^{-7} Torr) comprises a resistively heated Knudsen cell 12 loaded with a zinc diethyldithiocarbamate precursor powder (not shown) for the single source chemical vapour deposition (SSCVD). A silicon Si(111) substrate 19 is mounted on a sample holder 16 on a heater 100 and the epitaxial film (not shown) is formed on the substrate 19. The chamber 10 further comprises a view port 11, a port 13 to which a vacuum pump (not shown) is connected and a flexible flange 15 as part of a x,y,z manipulator 17 for the heater 100.

As illustrated in Figure 8, sublimed zinc diethyldithiocarbamate molecules 80 impinge on the heated substrate 19. In the diethyldithiocarbamate molecules 80, the zinc atom is in a similar environment to that of zinc in crystalline ZnS. The SSCVD growth of the ZnS epitaxial film 84 proceeds via the pyrolysis of $Zn[S_2CN(C_2H_5)_2]_2$ on the heated substrate 19 (400ºC):

$$Zn[S_2CN(C_2H_5)_2]_2 \rightarrow ZnS + C_2H_5NCS + (C_2H_5)_3NCS_2 \qquad (1)$$

C_2H_5NCS and $(C_2H_5)_3NCS_2$ decompose into by-products such as C_2H_4, CS_2 and $(C_2H_5)NH$ which are volatile in vacuum and therefore do not remain on the heated substrate 19 during the ZnS epitaxial film growth.

In this embodiment epitaxial film growth of ZnS was found on the Si (111) surface (lattice mismatch ~0.2%).

As shown in Figure 9, in one embodiment the growth of epitaxial films comprises the cleaning of the Si substrate (step 90), the heating of the Si substrate (step 92), the sublimation of the diethyldithiocarbamate precursor (step

94), the pyrolysis of the diethyldithiocarbamate molecules on the heated substrate (step 96) and the formation of the epitaxial ZnS film on the heated substrate (step 98).

The cleaning of the Si(111) substrates (step 90) in one embodiment comprises the sequence of steps outlined in Table 1.

1	annealing in oxygen	1050ºC	30 min
2	rinse in deionised H_2O	room temp (ultrasonic bath)	5 min
3	rinse in EtOH	room temp (ultrasonic bath)	5 min
4	rinse in Iso-propyl alcohol	room temp (ultrasonic bath)	5 min
5	N_2 blown dry		30 sec
6	$12H_2O$: $7NHF_4$: 1HF	room temp	10 min
7	rinse in deionised H_2O	room temp	1 min
8	N_2 blown dry		30 sec
9	$5H_2O$: 1HCl : $1H_2O_2$	80ºC, oil bath	10 min
10	rinse in deionised H_2O	room temp	1 min
11	N_2 blown dry		30 sec
12	$12H_2O$: $7NHF_4$: 1HF	room temp	10 min
13	rinse in deionised H_2O	room temp	1 min
14	N_2 blown dry		30 sec
15	$5H_2O$: 1HCl : $1H_2O_2$	80ºC, oil bath	10 min
16	rinse in deionised H_2O	room temp	1 min
17	N_2 blown dry		30 sec
18	$12H_2O$: $7NHF_4$: 1HF	room temp	10 min
19	rinse in deionised H_2O	room temp	1 min
20	N_2 blown dry		30 sec
21	$5H_2O$: 1HCl : $1H_2O_2$	80ºC, oil bath	10 min
22	rinse in deionised H_2O	room temp	1 min
23	N_2 blown dry		30 sec
24	NH_4F (40%) or HF (5%)	room temp	10 min

25	rinse in absolute EtOH	room temp	2 min
26	Mounting onto sample holder/heater 16		
27	loading into deposition chamber 10		
28	heating for removing surface contaminants	350ºC, vacuum (10^{-8} torr)	15 min

In will be appreciated, however, that other cleaning step sequences and different treatment times may be applied, which may e.g. comprise sputtering and annealing steps in the high vacuum deposition chamber 10 (Figure 1).

Film Characterisation

The resulting epitaxial films were characterised using X-ray photoelectron spectroscopy (XPS) and X-ray photoelectron diffraction (XPD).

Figure 2 shows an angle dependent XPD scan of the Zn $2p_{3/2}$ intensity distribution for ZnS epitaxial films at thicknesses ranging from ~5 to 2000Å. The film thicknesses were estimated using the intensity attenuating of the XPS Si substrate peaks. The XPD measurements were performed after subsequent SSCVD deposition cycles.

The XPD patterns exhibit an intense and broad peaks 20, 22, and 24 at $\theta=0º$ which are the result of forward-scattering of Zn $2p_{3/2}$ photoelectrons by neighbouring atoms. In ZnS, every zinc atom is surrounded by four sulfur atoms in a tetrahedral arrangement which results in either a cubic (sphalerite) or a, slightly distorted, hexagonal (wurtzite) structure.

The enhanced XPD intensities 20, 22, 24 at $\theta=0^{\circ}$ in curves a, b, and c of Figure 2 respectively therefore indicate that the film molecules have preferred orientation at the film-to-substrate interface and the Zn $2p_{3/2}$ photoelectrons are scattered by the sulfur neighbours perpendicular to the substrate.

As illustrated in Figure 3, the forward scattering enhancement 20, 22, 24 at $\theta=0^{\circ}$ in curves a, b and c of Figure 2 is likely the result of forward-scattering of $Zn2p_{3/2}$ photoelectrons emitted from the zinc atoms 30 at the sulphur atoms 32, which are positioned directly above the zinc atoms 30 at a distance of 2.3 Å in an ideal ZnS cubic crystal structure.

In Figure 4, a XPS wide scan 40 for a typical ZnS epitaxial film embodying the present invention is shown. In the curve 40 shown in Figure 4, the silicon substrate peaks can also be observed, which are not fully attenuated due to the thinness of the ZnS epitaxial film on which the XPS measurement shown in Figure 4 was performed. The chemical composition obtained from XPS scans such as the one shown in Figure 4 were in agreement with those obtained for a ZnS reference sample.

In Figure 5, the curve 50 shows the XPD measurement for the 2000Å thick film of curve c of Figure 2 after Ar^+ ion etching.

During the Ar^+ ion etching, highly energetic (2000 electron Volt (2keV)) impact on the film surface, resulting in a disordering of the crystallographic structure of the surface. In curve 50 of Figure 5, the XPD scan therefore does not indicate a significant forward scattering enhancement at $\theta=0^{\circ}$.

Energy dependent XPD was employed to probe the in-plane orientation of the film molecules. The sample position and angle remained unchanged while the energy of the incoming X-rays was varied.

The energy dependent XPD features shown in Figure 6 are a result of diffraction of S 2p photoelectrons in the ZnS atomic network. The photoelectron take-off angle was 19º with respect to the surface plane, i.e. the measurement was sensitive for crystallographic order within the plane of the substrate. As diffraction is a long range order process (diffraction of photoelectrons requires single crystalline surfaces) the observation of peaks 60, 62, 64 demonstrates that the film is of epitaxial quality.

As illustrated in Figure 7, the peaks 60, 62, 64 in the measurement shown in Figure 6 are due to the forward scattering of S 2p photoelectrons emitted from the sulphur atoms 70 at zinc atoms 72, which are the next neighbours of the sulphur atoms 70 in the $[11\bar{1}]$ crystallographic direction 74, along which the measurement shown in Figure 6 was measured. The distance between the sulfur atoms 60 and the Zn atoms 72 in an ideal ZnS cubic crystal structure is 2.3 Å.

In the following, a specific device application embodying the present invention will be described with reference to Figure 10.

Silicon is transparent at the typical telecommunications wavelength and it has been shown that Silicon-On-Insulator (SOI) structures can be used as waveguides. In these structures the wave is guided by a thin silicon layer on SiO_2.

Figure 10 illustrates the principles of an optical modulator design 100. The silicon 102 is partially replaced by an epitaxial ZnS layer 104 which acts as waveguide. A suitable AC voltage applied across the ZnS layer 104 alters the refractive index of the ZnS and it is therefore possible to modulate light 105 guided through the film directly.

The epitaxial ZnS layer 104 is grown on the remaining slightly doped (111) oriented silicon layers 106 which also comprises the bottom electrode. A thin metal film 108

(e.g. Cr) is deposited onto the ZnS film 104 and form the top electrode. Optical losses are dependent on the density of defects in the ZnS layer 104 and it is therefore of significant advantage that they can be grown single crystalline using the technology of the present invention.

It will be appreciated by a person skilled in the art that the present invention is not limited to that specific application, but other applications are possible, including for example in other optical modulator devices, optical waveguide devices, transistor and diode devices, blue light emitting devices, solar cells, and as coatings for infrared sensing, emitting, or transmitting devices.

In the claims that follow and in the summary of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprising" is used in the sense of "including", i.e. the features specified may be associated with further features in various embodiments of the invention.

In the claims that follow and in the summary of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprising" is used in the sense of "including", i.e. the features specified may be associated with further features in various embodiments of the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An epitaxial II-VI semiconductor film grown using single source chemical vapour deposition.

2. An epitaxial film as claimed in claim 1, wherein the epitaxial film comprises ZnS.

3. An epitaxial film as claimed in claim 2, wherein the ZnS is grown using zinc diethyldithiocarbamate as precursor for the single source chemical vapour deposition.

4. An epitaxial film as claimed in claim 2, wherein the ZnS is grown using $Zn(S_2CNR_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

5. A process as claimed in claim 4, wherein the number of carbon atoms in the alkyl group is in the range from 1 to 6.

6. A process comprising the steps of utilising single source chemical vapour deposition for growing an epitaxial II-VI semiconductor film on a substrate.

7. A process as claimed in claim 6, wherein the epitaxial film comprises ZnS.

8. A process as claimed in claim 7, wherein the process comprises the use of $Zn(S_2CNR_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

9. A process as claimed in claim 8, wherein the number of carbon atoms in the alkyl group is in the range from 1 to 6.

10. A process as claimed in claim 7, wherein the process comprises the use of zinc diethyldithiocarbamate as a precursor for the single source chemical vapour deposition.

11. A process as claimed in any one of claims 6 to 10, wherein the substrate comprises a silicon (111) substrate.

12. A substrate coated with a coating comprising an epitaxial II-VI semiconductor film grown using single source chemical vapour deposition.

13. A substrate as claimed in claim 12, wherein the substrate comprises silicon (111).

14. A substrate as claimed in claims 12 or 13, wherein the epitaxial film comprises ZnS.

15. A process for growing an epitaxial II-VI semiconductor film, the process comprising the steps of:

- cleaning a substrate,
- heating the substrate to a deposition temperature,
- the sublimation of a single source chemical vapour deposition precursor;
- the pyrolysis of the precursor molecules on the heated substrate; and
- the formation of the epitaxial film on the heated substrate.

16. A process as claimed in claim 15, wherein the substrate comprises silicon (111).

17. A process as claimed in claim 15 or 16, wherein the epitaxial film comprises ZnS.

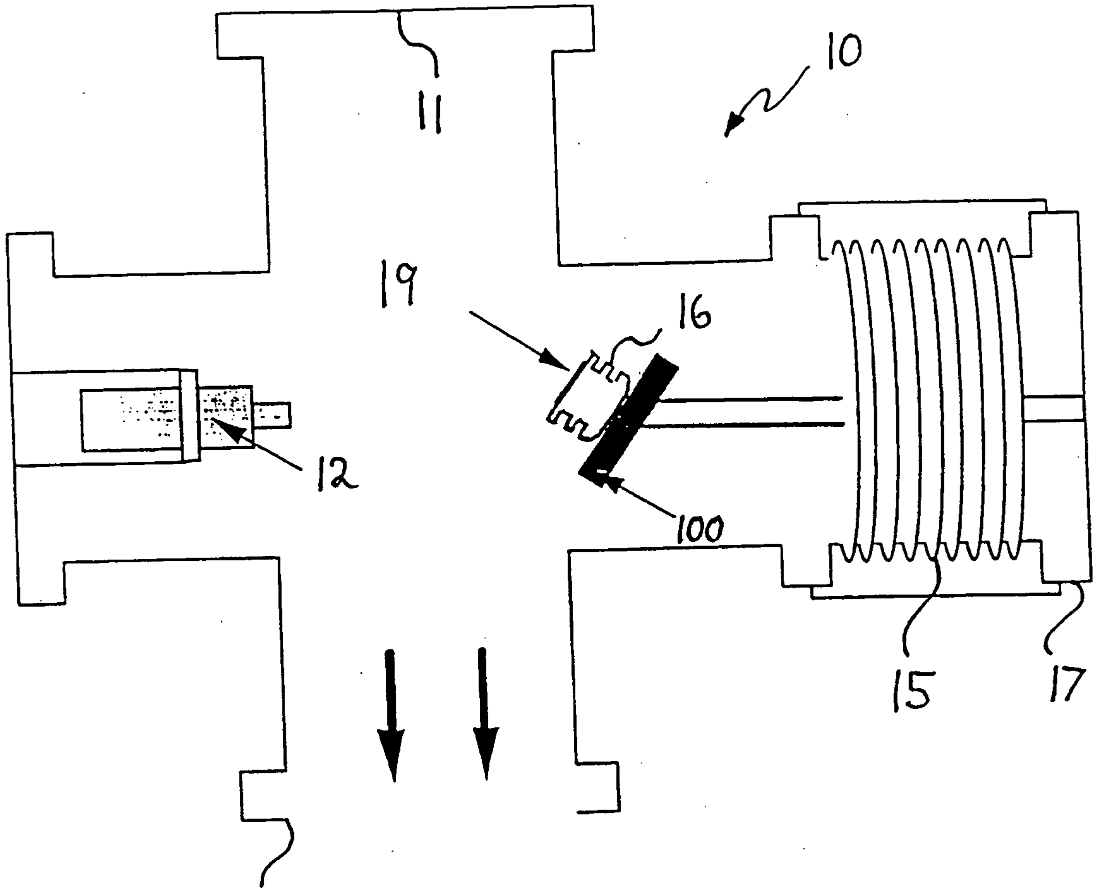

Figure 1

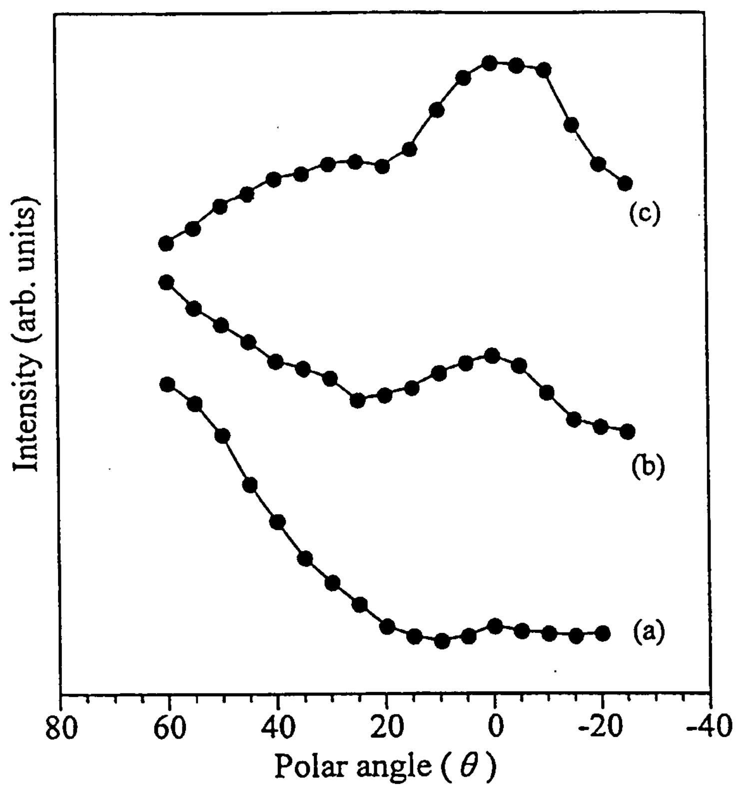

Figure 2

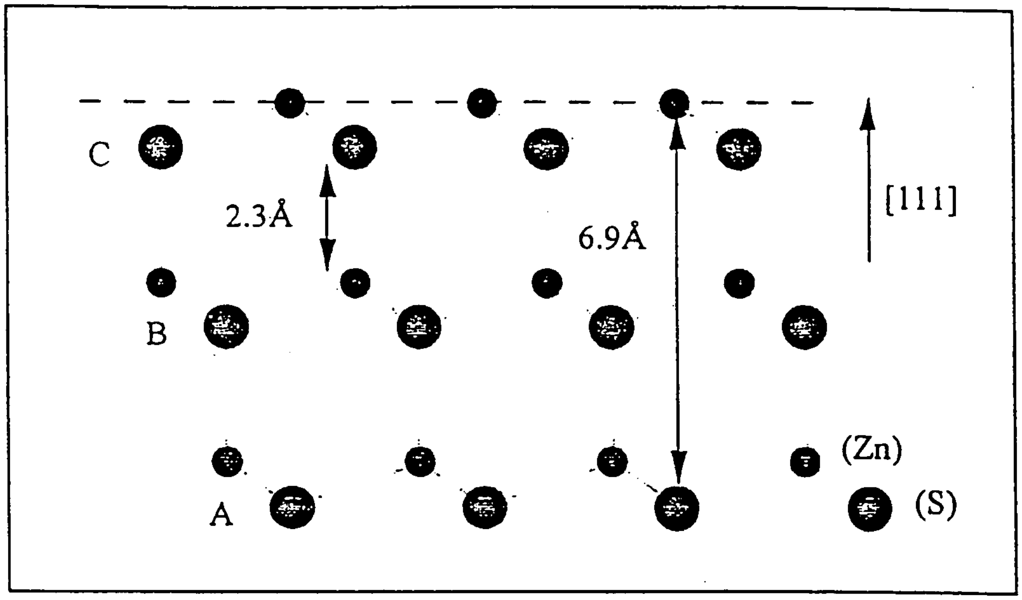

Figure 3

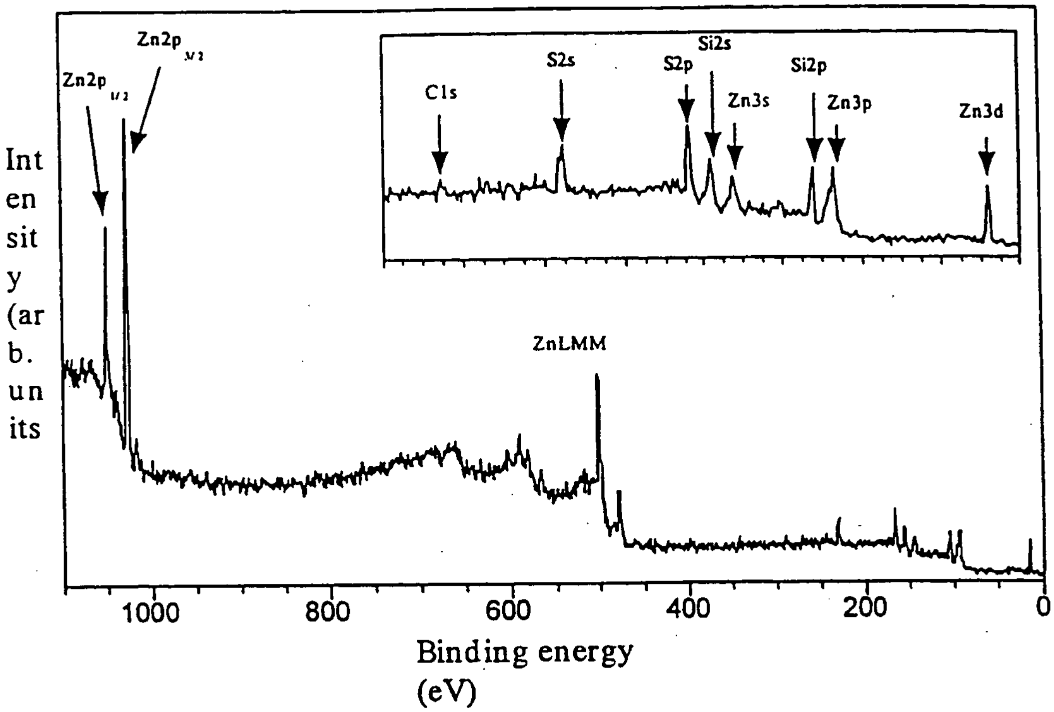
Zn2p 1/2
Zn2p 3/2
Int en sit y (ar b. un its
C1s
S2s
S2p
Si2s
Zn3s
Si2p
Zn3p
Zn3d
ZnLMM
1000
800
600
400
200
0
Binding energy (eV)

Figure 4

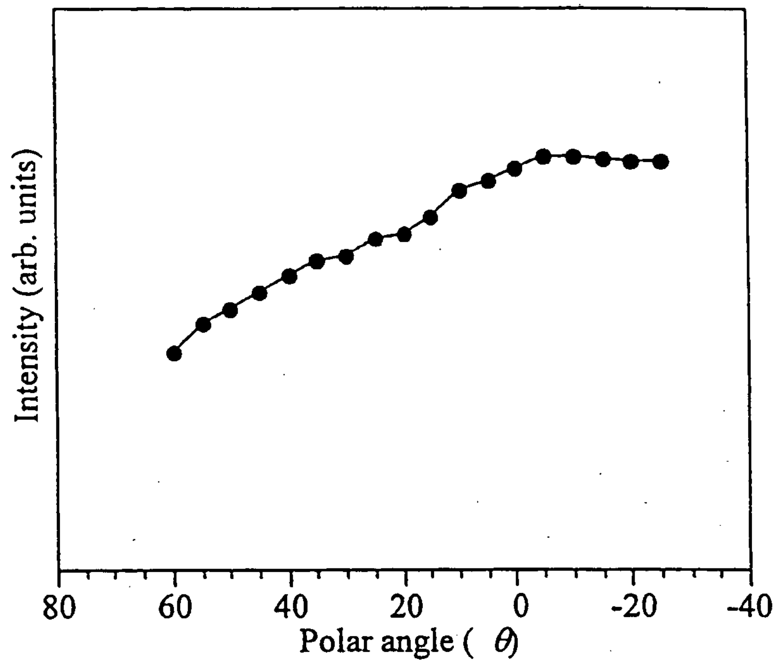

Figure 5

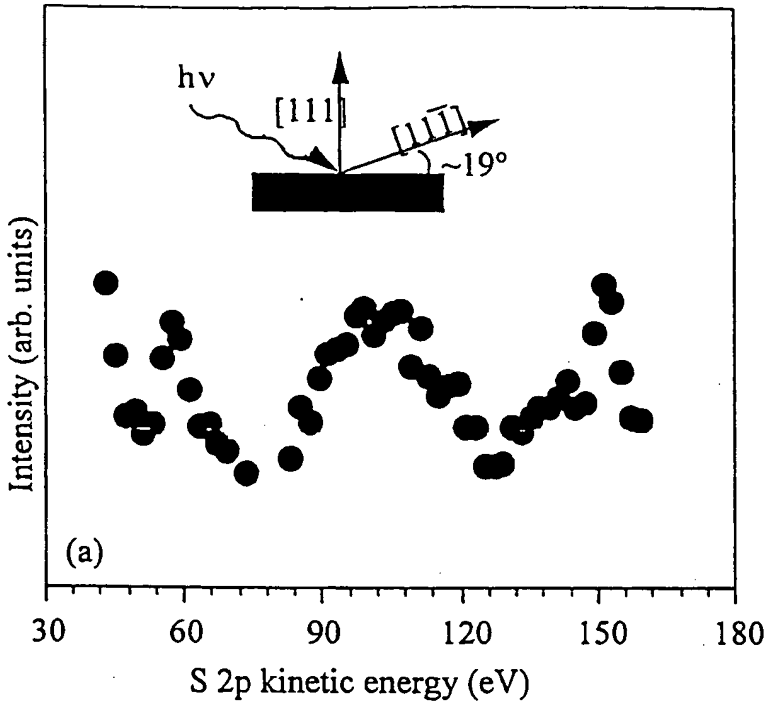

Figure 6

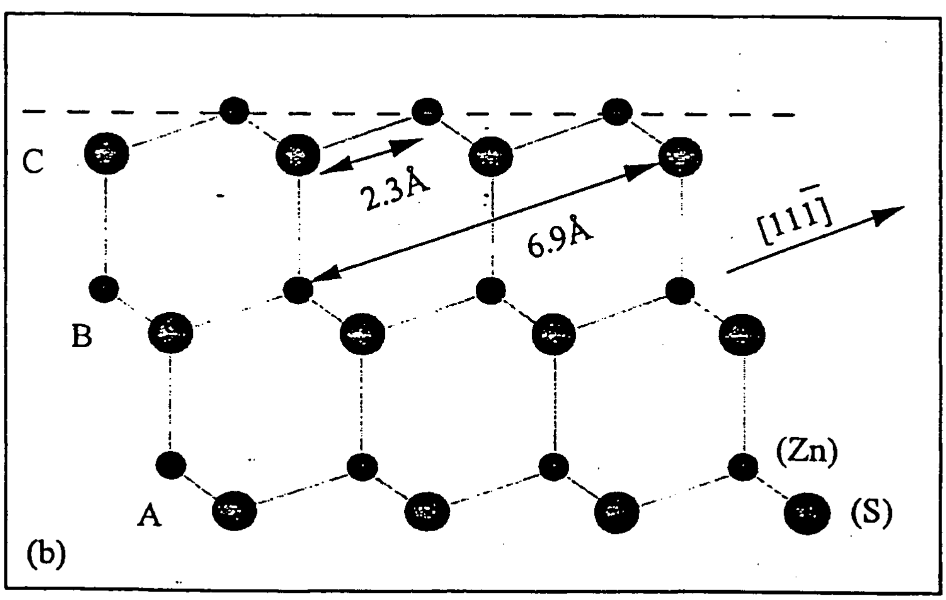

Figure 7

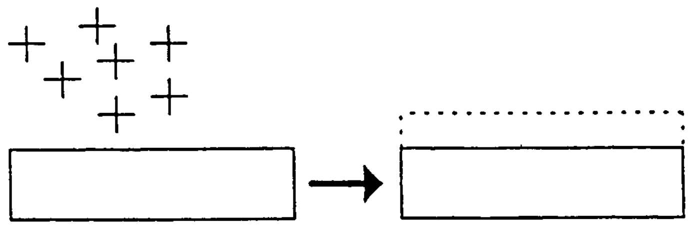

Figure 8

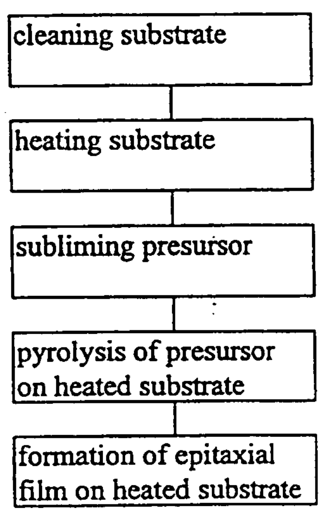

Figure 9

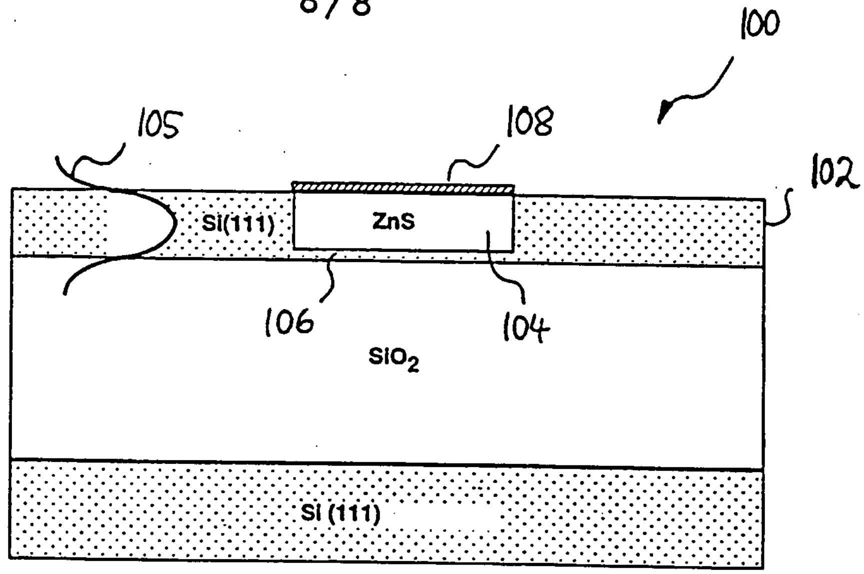

Figure 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00696

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: C30B 25/02, 29/48, H01L 21/365

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C30B 25/02, 29/48, C23C 16/30, H01L 21/365

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
dwpi IPC and (singl+ or vapo+) and (source+ or precurs+)
caplus dithiocarbamate and zinc and semiconductor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Metalloorganicheskaia Khimiia, 1, No.3, 1988 (Druz et al.) "Growth Epitaxial Films of Sulfides of Cadmium and Zinc from Dithiocarbamate Compounds $M(S_2CNEt_2)_2$ (M=Cd, Zn)", see pages 645 - 649.	1-17
X	Thin Solid Films, 271, 1995 (Nomura et al.) "Single-Source MOVPE Growth of Zinc Sulfide Thin Films Using Zinc Dithiocarbamate Compexes", see pages 4-7.	1-17
X	Journal Of The American Chemical Society, 119, No.16, 23 April 1997 (Cheon et al.) "Gas Phase Photochemical Synthesis Of II/VI Metal Sulfide Films…", see pages 3838-3839.	1-17

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 August 2000	22 AUG 2000

Name and mailing address of the ISA/AU	Authorized officer
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Journal of Crystal Growth, 97, 1989 (Jones et al.) "The Growth of CdS and CdSe Alloys by MOCVD using a New Dimethylcadmium Adduct" see pages 537-541	1
X	Derwent Abstract Accession No. 96-496203/49, Class E12, RU 2055948 C1,(AS SIBE INORG CHEM INST) 10 March 1996	1, 15-16
X	Patent Abstract of Japan, JP 11087747 A (MATSUSHITA DENCHI KOGYO KK) 30 March 1999 & JP 11087747 A	1-17

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. PCT/AU00/00696

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member
JP	11087747	NONE
RU	2055948	NONE
		END OF ANNEX